

The analytical solution of the Schrödinger equation in Born-Oppenheimer approximation for H_2^+ molecular ion

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An analysis of the analytical solution of the Schrödinger equation (which is a second order differential equation) for H_2^+ shows that the second linear independent solution of this equation is a square integrable function and therefore the ground state total wave function is a linear combination of two linear independent wave functions of different space symmetry: cylindrical and spherical. The wave function of cylindrical symmetry is well known. It has maxima at the positions of nuclei. The wave function of spherical symmetry and the corresponding spherical electron distribution, which exists at $R \neq 0$ and locates at the middle of the bond, represents a quasiatom of electron density of non-nuclear united atom. In the light of the new result the qualitative behavior of the ground state wave function and the electron density of H_2^+ has been reinvestigated. It is shown analytically that a transformation of the total molecular wave function with two maxima to that one with one maximum passes through a flat wave function. The presented three-dimension figures of the electron density visualize the spherical component of the total wave function and its transformation with increasing internuclear separation.

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The property and behavior of the ground state wave function of H_2^+ molecular ion is very important for quantum mechanics because it establishes our general representation on the quantum interaction in molecules. For this reason the ground state wave function and electron density of H_2^+ ion was investigated in many publications by using different approaches. However, an analysis of these results shows that there is a direct contradiction between them. This lead us to non-unique qualitative representation on a behavior of the ground state wave function.

Thus, from one hand side, from asymptotic properties of the total wave function follow that at the limit of a united atom the ground state wave function of H_2^+ transforms to the wave function of He^+ . Therefore, after some small R the H_2^+ wave function must have only one maximum at the middle of the bond. This is a basis of perturbation theory developed by Bethe for a calculation of the H_2^+ total energy at short R [1]. In this theory the H_2^+ wave function is approximated by the He^+ wave function located at the middle of the bond. The investigation of Bethe's perturbation theory shows that it works well up to $R = 0.05$ a.u. [2]. Other example, which displays an importance of a correct asymptotic of the total molecular wave function in the limit of a united atom was given in Ref. [3]. In this work it was shown that a representation of the molecular wave function as a linear combination of united and separated atoms wave functions results in significant improvement of the H_2^+ variational total energy calculated at short R .

From other hand side, from a solution of the Schrödinger equation in Born-Oppenheimer approxima-

tion in alliptic coordinates for H_2^+ given by Burrau [4] follows that the solution has two maxima at the position of two nuclei.

To clarify this question and to show that the second linear independent solution of the Schrödinger equation is square integrable function let us consider first the H_2^+ problem qualitatively. In the Born-Oppenheimer approximation the Hamiltonian of H_2^+ can be written as

$$H(R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{|r - R_A|} - \frac{1}{|r - R_B|} + \frac{1}{R} \quad (1)$$

where r is the vector of the electron; $R = |R_A - R_B|$ is the internuclear distance; R_A and R_B are the vectors of nuclei A and B ; and the electron and nuclei charges are equal to one. A parametric dependence of $H(R)$ on R shows that at the limit $R \rightarrow 0$ Hamiltonian (1) reduces to the Hamiltonian of the He^+

$$H(R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{2}{|r - R_A|},$$

while the H_2^+ total wave function transforms to the total wave function of the He^+ ion. At the limit $R \rightarrow \infty$ there is an equally probability that the electron can be located near nucleus A or B and thus forms H atom at the point A or B . Therefore, Hamiltonian (1) transforms to the Hamiltonian of the H atom

$$H(R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{|r - R_A|}.$$

The total molecular wave function in this case reduces to the wave function of the H atom.

Summarize the asymptotics of Hamiltonian (1) and follow to the *superposition principle* we can conclude that

the total wave function of H_2^+ molecular ion can be presented as a linear combination of three atomic wave functions

$$\Psi(R) = c_A(R)\Psi_A + c_B(R)\Psi_B + c_U(R)\Psi_U \quad (2)$$

where Ψ_A and Ψ_B are the wave functions of H atoms and Ψ_U is the total wave function of He^+ ion. In this expression each wave function Ψ_A , Ψ_B , and Ψ_U is located on a separated center. Therefore, we can see that consistent quantum mechanical consideration of H_2^+ problem results in a three-center problem with corresponding three-center representation of the total molecular wave function.

The use of representation (2) for the total molecular wave function in calculations of H_2^+ total energy with high precision at short R was advocated in Ref. [3]. At equilibrium distances the use two-center expansion instead three-center expansion (2) results in a small gap between the Hartree-Fock total energies of H_2 calculated by numerical methods and in conventional two-center LCAO approximation. In Ref. [5] was shown that the use of expansion (2) permits to remove this gap. These two examples together with the Bethe's perturbation theory [1] show that the expansion (2) is correct.

One of a particular interest of the present study consists in study of a transformation of the molecular wave function and electron density distribution with changing R from $R = 0$ to $R = +\infty$. Expression (2) together with a conventional assumption that a wave function and its derivatives are continuous functions gives us a solid basis for a consideration of such transformation.

From the consideration given above follows that if Ψ_A , Ψ_B , and Ψ_U are atomic wave functions then at $R = 0$ $c_A(0) = c_B(0) = 0$ and $c_U(0) = 1$, while at $R = +\infty$ $c_A(+\infty) = c_B(+\infty) = c_N$, where c_N is a normalization coefficient and $c_U(+\infty) = 0$. Now, taking into account a continuous property of $\Psi(R)$, which means that all coefficients in (2) and their derivatives are continuous functions on R , and suppose that a distribution of electron density is defined by a total wave function, we can derive two important statements:

a) for any small ε_0 it is possible to find such R_0 that when $R < R_0$ the total molecular wave function can be presented as $\Psi(R) = c_U(R)\Psi_U + O(\varepsilon_0)$. This means that at sufficient small R the total molecular wave function and corresponding distribution of electron density must have only one maximum. As a consequence, a transformation of the molecular wave function and the electron density with two maxima to those with one maximum passes through a flat wave function and corresponding flat electron distribution.

b) the spherical component Ψ_U of the total molecular wave function $\Psi(R)$ exists in molecule at $R \neq 0$. It is the wave function of a united atom and in molecule it represents the electron density of a non-nuclear united atom

or quasiautom. The spherical component of the molecular wave function and appropriate electron distribution located at the middle of the bond can be observed in molecule at some R .

Now, follow to Burrau [4], we consider the Schrödinger equation in Born-Oppenheimer approximation for H_2^+ in elliptic coordinates: $\xi = (r_1 + r_2)/R$ and $\eta = (r_1 - r_2)/R$. In these coordinates, the wave function for the Σ ground state can be presented as $\Psi = X(\xi, R)Y(\eta, R)$, where $X(\xi, R)$ and $Y(\eta, R)$ satisfies the following equations:

$$\begin{aligned} (\xi^2 - 1) \frac{d^2 X}{d\xi^2} + 2\xi \frac{dX}{d\xi} + \left(\frac{1}{2}ER^2\xi^2 - 2R\xi + A \right) X &= 0 \\ (1 - \eta^2) \frac{d^2 Y}{d\eta^2} - 2\eta \frac{dY}{d\eta} - \left(\frac{1}{2}ER^2\eta^2 + A \right) Y &= 0 \end{aligned} \quad (3)$$

and E and A is energy and separation constant to be determined. It needs to note here that the elliptic coordinates are undefined at $R = 0$ and therefore the equations given above are valid only for $R > 0$.

To clarify behavior of the total wave function at the middle point it is sufficient to investigate behavior of $Y(\eta, R)$ and $Y'(\eta, R)$ at $\eta = 0$ and at small R . In this case equation (3) transforms to an ordinary differential equation of the second order

$$\frac{d^2 Y}{d\eta^2} - AY = 0$$

The general solution of this equation is as a linear combination of two linear independent solutions:

$$Y(0, R) = c_1(R) \exp\left(-\sqrt{A}|\eta|\right) + c_2(R) \exp\left(\sqrt{A}|\eta|\right) \quad (4)$$

that must be taken at $\eta = 0$. Despite of this limitation we can conclude that the algebraic structure of the total wave function will be preserve at the vicinity of this point because of the wave function is continuous function. This permits us to compare the expressions (4) and (2). From this comparison follows that the first solution of spherical symmetry corresponds to the wave function of a united atom which has a maximum on η at $\eta = 0$, while the second one of cylindrical symmetry has *no local minimum* on η at $\eta = 0$ and is formed by the linear combination of wave functions of separated atoms. On this basis we can conclude that the both linear independent solutions are square integrable functions. Therefore, the general solution of the Schrödinger equation indeed is a linear combination of two linear independent solutions that represent two different quantum objects.

It is interesting to note that Eq. (4) is similar to the one-dimension Schrödinger equation for an electron in a central potential

$$\frac{d^2 \Psi}{dx^2} + (V - E)\Psi = 0$$

A formal solution of this equation is also a linear combination of two linear independent solutions

$$\Psi = d_1 \exp\left(-\sqrt{E-V}|x|\right) + d_2 \exp\left(\sqrt{E-V}|x|\right)$$

However, in this case the second solution is not square integrable function. Therefore, it is excluded from a consideration.

Now, suppose that the coefficients in (4) are continuous functions, we can conclude that at $R \rightarrow 0$ Eq. (4) can be smoothly transformed to the well-known one-dimensional atomic wave function only if $c_2(R) \rightarrow 0$ (because of this component transforms to the not square integrable function) and $c_1(R)$ becomes equal to a normalization constant of the united atom wave function.

The first derivative of (4) on η taken at $\eta = 0$ is

$$\frac{dY(0, R)}{d\eta} = -\sqrt{A} [c_1(R) - c_2(R)].$$

It is negative at small R because of $c_2(R) \rightarrow 0$ at $R \rightarrow 0$. This means that $Y(0, R)$ has a maximum. With increasing R and growing $c_2(R)$ the first derivative becomes equal to zero and after that it can be positive or negative in dependence on the values of the coefficients. At large R when coefficient $c_2(R)$ becomes dominant only "minimum" can be observed at $\eta = 0$.

In the light of the analytical solution of the Schrödinger equation given above it needs to comment the results presented in [6, 7]. Our analysis will base on the fact that the Schrödinger equation is a second order differential equation and its general solution is a linear combination of two linear independent solutions. An additional requirement for this equation is that the solutions must be square integrable functions. Otherwise they should be excluded from a consideration.

An analysis of the publications [6, 7] shows that in these studies only one solution of cylindrical symmetry (that can be called classical) of the Schrödinger equation has been taken into consideration, while the existence of the second solution and its analytical properties was not discussed. This means that an *implicit assumption* that the second solution is a not square integrable function has been used in these works. However, the present study gives strong evidences that the second solution of spherical symmetry (that can be called quantum or quasiautomic) is a square integrable function and therefore it must be taken into consideration also.

A proof that the results presented in [6, 7] have been obtained only for the classical component of the total wave function but not for the total wave function follows directly from the fact that the statement (v) of *Theorem 1* [7] that the wave function has no local minimum is a simple consequence of the analytical solution given above.

To visualize the transformation of the total wave function $\Psi(R)$, the electron densities of H_2^+ at different R

have been calculated in quantum mechanical variational calculations by using the Gaussian 98 program [8]. These calculations can be considered also as an independent verification of the analytical results presented above because only the nuclear centered basis of *15s6p5d4f3g2h1i* Gaussian spherical functions was employed. It was formed from an optimized set of *15s* functions supplied by polarization functions taken from pV7Z basis for *H* atom [9]. A quality of the variational wave function was controlled by comparing obtained variational total energies with those ones calculated by the program [10] and presented in Table I. A uniform deviation of the variational total energies from the numerical ones, which is equal to $1.2 \cdot 10^{-7} E_h$, points out that the employed basis results in a high quality variational wave function.

The calculated electron densities of H_2^+ at a few R are presented on Fig. 1. At the beginning of a consideration we can note that at $R = 0$ the electron density is spherical. Then, at small R , the spherical distribution continuously transforms to an ellipsoidal distribution with one maximum. This distribution is presented on Fig. 1 at $R = 0.008 \text{ a.u.}$ Further increasing R results in appearing a flat surface on the electron density distribution at $R = 0.010 \text{ a.u.}$ given on Fig. 1 followed by appearing the two maxima at the positions of two nuclei and a transformation of the ellipsoidal electron density distribution to a cylindrical one. Appropriate cylindrical electron density at $R = 0.012 \text{ a.u.}$ is presented at Fig. 1. Subsequent increasing R reveals the existence of the spherical component of electron density with additional maximum located at the middle of the bond. The three-dimension figure of the electron density with a quasiautomic is presented on Fig. 1 at $R = 0.019 \text{ a.u.}$

To show that a quasiautomic solutions exist in any molecular system the electron density distribution has been investigated in all homonuclear diatomic molecules of the first-row elements. The spherical symmetry electron density distributions (quasiautoms) arisen from the second linear independent solutions and located at the middle points have been observed in all molecules. At some internuclear separations quasiautomic solutions result in additional maxima on a profile of electron densities along the molecular axis. An example of such electron density distribution in Li_2 at 5.0 a.u. ($R_e = 5.051 \text{ a.u.}$ [11]) is presented on Fig. 2. The quasiautomic located at the middle point is explicitly recognizable on this figure. The electron density distribution was obtained in *ab initio* calculations with cc-pVQZ Gaussian basis set [12] by quadratic configuration interaction method as realized in Gaussian 98 program. Details of this study will be given elsewhere [13].

The qualitative behavior of electron densities presented on these figures is fully consistent with that one, which follows from the analytical solution of equation (4) and a qualitative consideration of the asymptotic properties of the Hamiltonian (1) given above. Despite of using only

nuclear centered basis, that corresponds to the cylindrical solution, the spherical component of the molecular wave function or the other linear independent solution of the Schrödinger equation and the corresponding spherical electron distribution located at the middle of the bond was formed in accordance with theory of the second order differential equation to keep asymptotic and continuous properties of the total molecular wave function.

Thus, the analytical solution of the Schrödinger equation given in the present investigation shows that the ground state total wave function of H_2^+ is a linear combination of two linear independent wave functions of spherical and cylindrical symmetry. The former one represents a quasiatom of the electron density of non-nuclear united atom and is responsible for appearing a spherical distribution of the electron density and an additional maximum on a profile of the electron density along the internuclear axis at some R .

TABLE I: The total energies (in Hartree) of the H_2^+ molecular ion.

R (a.u.)	E_{tot} (var.)	E_{tot} (numer.*)
0.008	123.00016807	123.00016795
0.010	98.00026148	98.00026136
0.012	81.33370830	81.33370818
0.019	50.63250557	50.63250545

* - Calculated by the program [10].

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- [1] H. Bethe, in *Handbuch der Physik* Eds. H. Geiger and K. Scheel (Springer-Verlag, Berlin, 1933), Vol. 24/1, p. 527.
- [2] H. Wind, *J. Chem. Phys.* **42**, 2371 (1965).
- [3] A. Dalgarno and G. Poots, *Proc. Phys. Soc. (London)* **67A**, 343 (1954).
- [4] Ø. Burrau, *Kgl. Danske Videnskab. Selskab. Math.-fysiske Meddel.* **7**, No. 14, 1 (1927).
- [5] A. V. Mitin, *Phys. Rev. A* **62**, 010501(R) (2000).
- [6] T. Kato, *Commun. Pure Appl. Math.* **105**, 151 (1957).
- [7] T. Hoffmann-Ostenhof and J. D. Morgan III, *J. Chem. Phys.* **75**, 843 (1981).
- [8] Gaussian 98, Revision A.11.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2002.
- [9] D. Feller and K. A. Peterson, *J. Chem. Phys.* **110**, 8384 (1999).
- [10] F. Sattin, *Comp. Phys. Comm.* **105**, 225 (1997).
- [11] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules*, van Nostrand-Reinhold (1979).
- [12] T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- [13] A. V. Mitin, to be published.

FIGURE CAPTIONS

Figure 1: The total electron densities of H_2^+ molecu-

lar ion at different internuclear distances.

Figure 2: The total electron densities of Li_2 at 5.6 a.u.

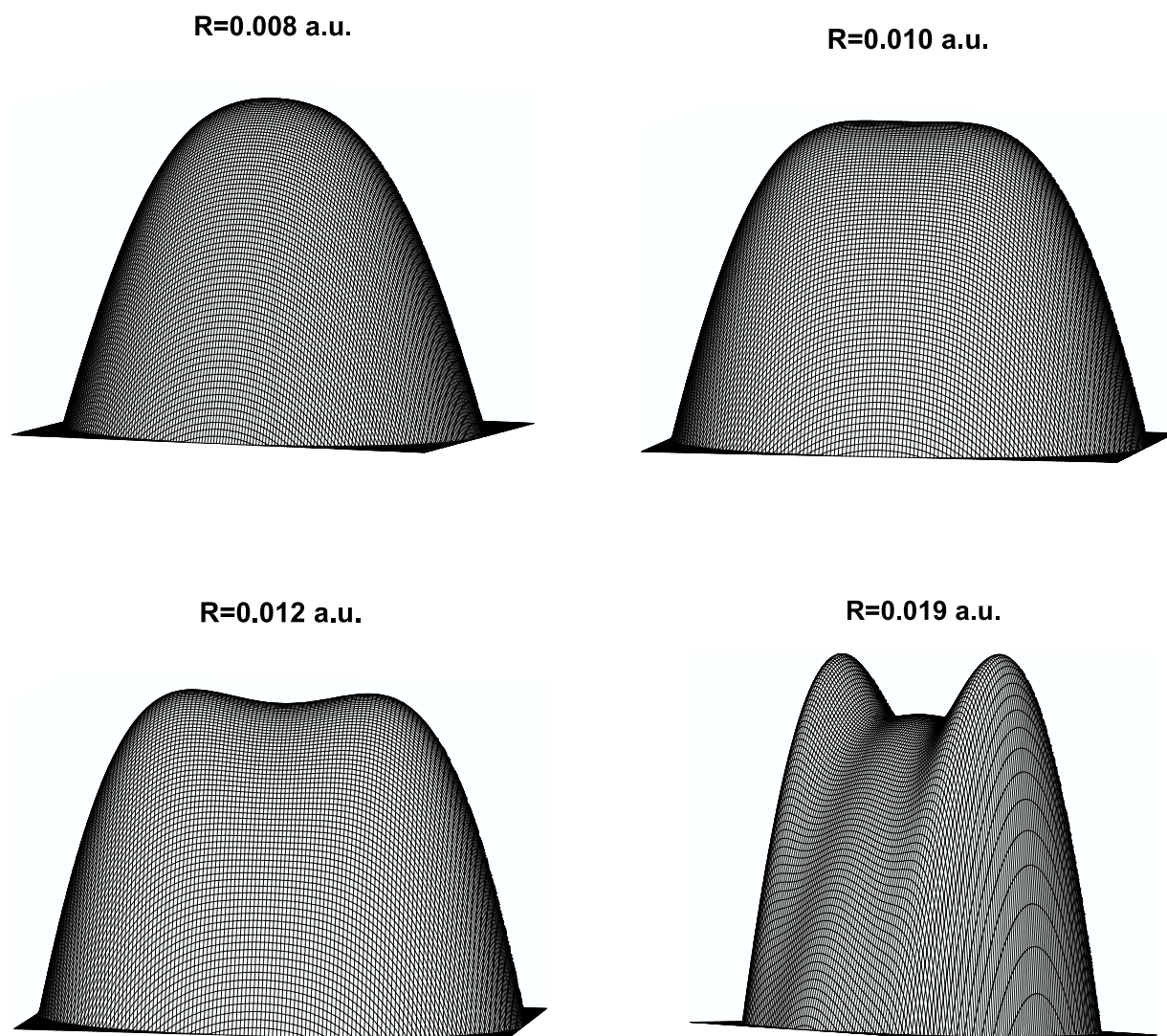


Figure 1. The total electron densities of H_2^+ molecular ion at different internuclear distances.

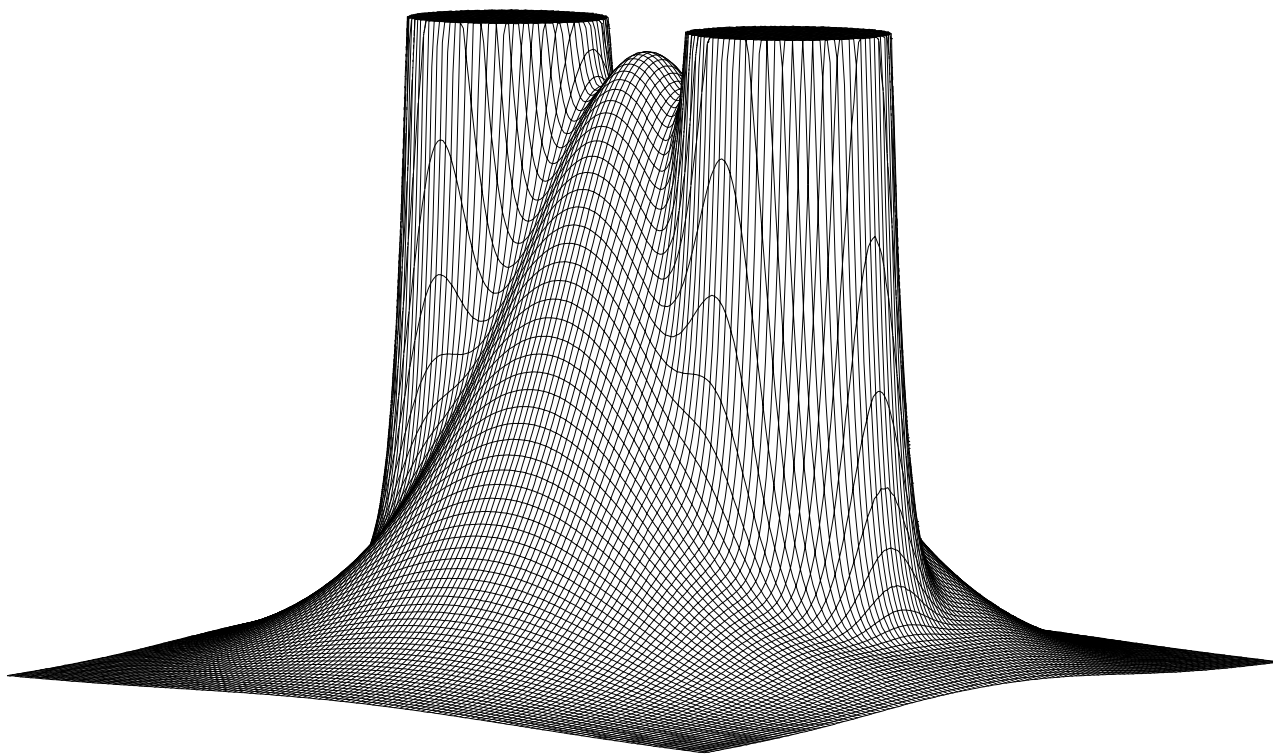


Figure 2. The total electron densities of Li_2 at 5.0 a.u. internuclear separation.